Mono-Molecular Adsorbed Layers of Water on YSZ, their Point Defects and Ionic Conduction

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INTRODUCTION

Water adsorbs chemically on oxides even at rather elevated temperatures forming OH groups on the oxide surface. This occurs at the cathode side of a fuel cell due to residual humidity in the air feed to the cathode. At the anode exposed to hydrogen OH groups are also formed on the oxide. Therefore in both electrodes any analysis of the elementary steps has to take into consideration the coverage of the oxide surface by OH groups and the mobility of defects in this layer (1).

Adsorption of water can be controlled to form one, two or a few mono-molecular layers on solids by proper choice of temperature and water vapor pressure. It turns out that the electrical conductivity and weight of the chemisorbed and physisorbed layers can be measured and used to investigate the layers properties, including enthalpies of adsorption, and formation of point defects in these layers, and mechanism and enthalpy of migration of the defects. EMF measurements can be performed using the mono-molecular layer to establish the existence of ionic conduction in the layer. Favorable conditions for achieving this are: solid electrically insulating grains with large surface area (grain size <1μm). For large area grains the weight of the adsorbed gas can be followed by thermogravimetry (TGA) which can be used in combination with electrical conductivity measurements and EMF measurements for a comprehensive analysis of the adsorbed layer.

We report here on experiments on one, two and a few mono-molecular water layers adsorbed onto Y_2O_3 stabilized ZrO_2 (YSZ) using electrical conductivity, EMF measurements and TGA measurements and the characterization of these layers (2). We show that at temperatures below ~600^{O}C chemisorption of water on YSZ becomes significant and therefore may affect the cathode properties. We show also that exposure to hydrogen inhibits water chemisorption by forming its own OH groups with the surface oxygen which may affect the anode reaction.

RESULTS AND DISCUSSION

Fig. 1 exhibits the resistance of humid powder (thin line) and dry powder (heavy line) as a function of temperature. The resistance of the dry powder is about an order of magnitude higher than that of the wet powder. The increase in resistance as T decreases below 450^{o}C towards 150^{o}C is explained by a lower defect concentration and defect mobility in the OH layer. The flattening off and then the decrease in the resistance as T is lowered below 150^{o}C is explained by physisorption of water forming one or more mono-layers on top of the chemisorbed one.

Fig. 2 exhibits the mass vs. T. The reference weight is that at 600^{o}C, taken as zero, as adsorption is then negligible. A two stage adsorption process is seen, the chemisorption one at elevated T and the physisorption of multi mono-layers of water, at low T.

CONCLUSIONS

Water adsorbs on YSZ up to elevated temperatures (~600^{o}C) and allows the ionic conduction of protons. It may also facilitate a mechanism for oxygen ion conduction.

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REFERENCES

1. A.Bieberle, L.P. Meier and L.J. Gauckler, preprint.
2. S. Raz, K. Sasaki, J. Maier and I. Riess, Solid State Ionics, (in print).

Figure 1. Resistance of YSZ powder vs. T. Heavy line: dry powder. Thin line: powder with adsorbed water.

Figure 2. TGA of water adsorption vs. T. ● Theory.